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VENUS CLOUDS: A DIRTY HYDROCHLORIC ACID MODEL

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The spectral and polarization data for Venus are consistent with micron-sized, aerosol-cloud particles of hydrochloric acid containing soluble and insoluble iron compounds, whose source could be volcanic or crustal dust. The ultraviolet features could arise from variations in the Fe - HCl concentration in the cloud particles.

In spite of four successful penetrations of the atmosphere of Venus by Venera entry probes and two flybys by Mariner spacecraft the question of the composition of the clouds of Venus remains controversial. Many materials have been suggested as the dominant component of the clouds, including H_2O liquid or ice, partially hydrated ferrous chloride, ammonium chloride, mercury halides, carbon suboxide, and dust (1 - 7),

Observations

Any proposed substance must be consistent with the following observations. Theoretical analyses by Hansen and Arking (8) of the polarization data of Coffeen and Gehrels (9) have provided extremely strong evidence concerning the physical nature of the cloud particles. The particles are spherical, and thus are almost certainly liquid, have indices of refraction of $1.45 \pm .02$, and exist in a narrow size distribution with radii close to 1μ . Because of the detailed matching of the theoretical model to the observed polarization-phase-wavelength curves it is unlikely that Hansen and Arking's conclusions are seriously in error.

The spectrum of Venus is shown in Figures 1 and 3. The cloud particles absorb strongly in the near IR over the $3 - 5\mu$ wavelength region and also have absorption features in the visible at $0.4 - 0.6\mu$ and in the UV below 0.4μ . For wavelengths longer than about 5μ the radiation is primarily due to thermal emission, and it is difficult to know whether the spectral features are to be interpreted as absorption or emissivity bands. For wavelengths shorter than about 0.3μ the radiation can be accounted for almost entirely by Rayleigh scattering from gas above the clouds, and little information can be obtained about the absorbing properties of the cloud particles in this spectral region (10). Several strong absorption bands of atmospheric CO_2 in the $1 - 3\mu$ range make it difficult to ascertain the exact spectrum of the clouds in the near IR.

The only gases which have been detected spectroscopically from Earth in the atmosphere of Venus are CO_2 , H_2O , CO , HCl , and HF . The mixing ratios of the latter four gases at the level in the atmosphere where the CO_2 pressure is approximately 0.2 atm and the temperature of the order of 250°K (altitude approximately 60 km) are of the order of 10^{-4} to 10^{-6} , 10^{-4} , 10^{-6} and 10^{-8} respectively (3, 16). By contrast, the Venera probes measured H_2O mixing ratios of 10^{-3} to 10^{-2} . It is presently not clear how these conflicting sets of data are to be reconciled, except that the H_2O and CO_2 Earthbased determinations may refer to different positions in the atmosphere and to different times.

The preceding observations argue against most of the proposed substances as the major constituent of the clouds. The requirement of being liquid eliminates ice, ferrous chloride, ammonium chloride and dust. The narrow size distribution implies a condensable substance, arguing against the chlorides and dust. Ferrous chloride has a prominent Fe^{+2} absorption band at 1.0μ which is not observed in the Venus spectrum (12). Although H_2O water and ice, ferrous chloride and ammonium chloride absorb strongly at 3.0μ they become translucent again past 4.0μ , and clouds consisting of micron-sized particles of these substances would be bright at long wavelengths. The spectra of C_3O_2 and mercury halides do not match the detailed spectrum of Venus (3,6). Of all the proposed substances, only C_3O_2 has a refractive index close to 1.45. The albedos of volcanic dusts are too low for the clouds to consist primarily of this material.

The pressure of H_2O vapor in the atmosphere, as determined by Earthbased observations, is too low by significantly more than an order of magnitude to be in equilibrium with liquid water or ice at the 250°K level. However, if the Venera mixing ratios are correct then water clouds would have no difficulty in forming. Recent analyses of the Mariner 5 radio occultation data (17) indicate that the temperature profile of the Venus atmosphere is consistent with the presence of a condensing component at latitudes of 60 to 75 km. An H_2O mixing ratio of 10^{-4}

would allow water clouds to exist at the 75 km altitude ($T=210^\circ\text{K}$, $p=10^{-2}$ atm). The haze or cloud layer apparently extends to 120 km (18); between 75 and 120 km the temperature may be well below 200°K (17, 18) and water clouds would be stable for mixing ratios as low as 10^{-5} .

The IR Spectrum of Hydrochloric Acid

The spectra of water and 6M HCl acid are shown in Figure 2. Except for minor differences the spectrum of ice is similar to that of liquid water. The changes caused by the addition of HCl are due mainly to the hydronium ion OH_3^+ in the acid (19, 20), so that the addition of any strong acid to water results in a similar spectrum. Strong bases, ^{but not salts,} have a somewhat similar, but less pronounced, effect. The most striking change is the series of wide, overlapping OH_3^+ bands which keep the transmissivity of the acid solution low over the entire range of wavelengths from 3μ to beyond 16μ . Thus the low reflectivity of Venus in the 3 - 5μ range would be accounted for if OH_3^+ ions are abundant in the clouds. Lewis (4) has shown that the relative abundances of HCl and H_2O vapor observed in the atmosphere of Venus requires that any liquid in equilibrium with these gases will be a hydrochloric acid solution of the order of 25% by weight ($\sim 5-7$ M/l). Terrestrial volcanic exhalations contain abundant SO_2 . Therefore, possible alternatives to HCl could be H_2SO_3 or H_2SO_4 . However, SO_2 vapor has not been detected spectroscopically on Venus. Thus the most probable additive to the clouds on Venus is HCl.

In the acid the bands at 1.5 and 1.9μ have been decreased and widened and the continuum absorption increased, making these bands difficult to detect spectroscopically. Thus, an objection to ice and water clouds ^{involving these bands} raised by Rea and O'Leary (21) is further weakened, since the objection is not particularly important for cloud particles as small as 1μ . At 8μ the acid spectrum has a broad band which is not present in water and which corresponds to a minimum in the thermal spectrum of Venus.

Although a detailed scattering calculation remains to be done, the IR spectrum of hydrochloric acid appears to be compatible with the spectrum of Venus, in contrast

with pure water or ice. If this identification is correct, ice clouds will probably be much rarer on Venus than on Earth, since the addition of HCl to water depresses the freezing temperature to below 200°K for 6M HCl (4).

The UV Band of Venus

Hydrochloric acid has an extremely weak absorption band at 0.28μ . However, none of the observed constituents of the Venus atmosphere absorb appreciably in the $0.3 - 0.6\mu$ region. Therefore, it is necessary to resort to indirect arguments to account for the yellowish color of the clouds. Terrestrial clouds and aerosols form by nucleation onto both soluble and insoluble substances, and thus are not composed of perfectly pure H_2O . The compositions of terrestrial cloud nuclei are not well known, but analyses (22, 23, 24) of aerosol residues reveal three types of substances: NaCl from ocean spray, ammonium and sulfate ions and other materials primarily from industrial sources, and natural dust from volcanoes and the crust. Because of unfavorable surface conditions the first two sources will presumably not be present on Venus. However, because of the high surface temperature, volcanoes should be even more prevalent on Venus than on Earth. Volcanic dust has been estimated to reach altitudes greater than 60 km on Earth (25). Other finely-divided solids from the crust could be carried into the stratosphere by turbulence.

Residues of terrestrial stratospheric aerosols include Si, S and Fe (22); no Ni is detected, indicating the source of the Fe is not meteoritic. Volcanic dust which finds its way into the stratosphere of Venus would be readily attacked by the hydrochloric acid clouds. Volcanic glass is especially susceptible to acid leaching because of the high density of solid state defects. It has been shown that glass in lunar soil is strongly attacked by hydrochloric acid and that all of the cations which are abundant in the lunar soil are also present in the solute (27). Thus, if the crust of Venus is similar to the crusts of the Earth and Moon, ions of the following elements should be found both as solid nuclei and in solution in the Venus aerosols: Si, Al, Ca, Fe, Mg, Na, K, Ti, plus smaller amount of Cr, Mn, and V.

Because of the much greater chemical activity of hydrochloric acid compared with water, the concentrations of these ions should be much greater in Venus droplets than in terrestrial aerosols.

The coloration of terrestrial and lunar rocks and minerals is due almost entirely to absorption bands associated with the transition elements Fe, Ti, Cr, Mn, and V, with Fe being by far the most important because of its geochemical abundance. The Fe^{+3} ion has strong absorption bands in the 0.2 - 0.4 μ spectral region, and the yellow or red color of most iron compounds is due to these bands. The spectra of several iron-bearing materials are shown in Figures 2 and 3.

In spite of the fact that the atmosphere of Venus is slightly reducing, some Fe^{+3} would be expected due to oxidation by oxygen from the photodissociation of CO_2 and from thermal oxidation reactions of the type, $\text{FeO} + \text{CO}_2 \rightleftharpoons \text{Fe}_2\text{O}_3 + \text{CO}$, which would take place at the surface (30). Using a simple, two-stream scattering model for an optically-thick cloud layer and the absorbances of ferric salt solutions measured on a Carey 14 spectrophotometer, I estimate that ferric ion concentrations of the order of 0.3 mole/liter will account for the edge at 0.4 μ in the Venus spectrum and the yellow color of Venus clouds. The 0.24 μ ferric band, ^{shown in Figure 3,} is probably unobservable because of atmospheric Rayleigh scattering. Ferrous iron Fe^{+2} would also be expected to be abundant in the Venus clouds. However, this ion has only a weak band at 1.0 μ , and much more ferrous than ferric iron could be present without causing a detectable band.

The position of the near-UV ferric bands depends on the type and normality of the solvent. In water or in weak hydrochloric acid the ferric ion is complexed by H_2O molecules, resulting in a band at 0.30 μ . As the HCl concentration increases, complexes of FeCl^{+2} and FeCl_2^{+1} become significant and the band shifts to 0.34 μ . At concentrations above about 6M HCl the dominant complex is FeCl_4^{+1} , and the band splits into two components centered at 0.31 and 0.36 μ . In FeCl_3 salt the band is at 0.40 μ . In H_2SO_4 the ferric band is at 0.30 μ .

However, a

The reflection spectrum of Venus is poorly-known in the UV. ~~the~~ spectrum obtained by Glushneva at a phase angle of 45° (28), shown in Figure 3, is suggestive of a minimum at 0.34μ . Clearly, more high-precision observations of Venus in the near-UV are necessary. Such observations are extremely important because they could confirm the presence and abundance of Fe, HCl and liquid H_2O in the clouds of Venus, as well as indicating the type and normality of the acid.

The Visible Band of Venus

When surrounded by anions all of the transition element cations have absorption bands in the visible and near-IR due to d-electron transitions (31). For instance, Ti^{+3} has a band at 0.50μ . However, these bands are relatively weak, and it is doubtful whether any of them could account for the 0.5μ minimum in the Venus spectrum without the $1.0\mu Fe^{+2}$ band also being prominent. Much stronger electron-transfer bands can occur in the visible when two multivalent transition element ions are sufficiently close together that their d-orbitals overlap (32, 33). The intensity of this type of band depends on the product of the concentrations of the ions; the wavelength depends on the degree of overlap and on the nature and structure of the surrounding ions.

Because of the abundance of iron the Venus 0.5μ band is most probably a $Fe^{+2} - Fe^{+3}$ electron-transfer band, although if Ti is as abundant in the crust of Venus as it is in the lunar maria, a $Fe^{+2} - Ti^{+4}$ band may also be involved. In the Venus aerosols conditions appropriate for electron-transfer bands probably would not occur in the aqueous state because the solutions would have to be too concentrated. More favorable conditions would occur in precipitates involving iron complexed with ^{oxygen,} ammonia, chloride, carbonate or other ions, and in the insoluble portion of the aerosol nuclei. An example of a solid-state, electron-transfer band in the visible spectrum of an artificial basaltic glass containing Fe^{+2} , Fe^{+3} , and Ti^{+4} is shown in Figure 2. In this spectrum the tails of strong bands of Fe^{+3} and Ti^{+4} in the far UV are also prominent, but the $1.0\mu Fe^{+2}$ band is extremely weak, and no band is present at 0.34μ .

The Index of Refraction

The index of refraction of the upper Venus clouds is close to 1.45 (8), whereas the index of refraction of a 6M HCl solution is approximately 1.39 and is only weakly dependent on temperature (34). However, most solutes have the effect of raising the index of refraction of an aqueous solution by the order of .01 - .03 per mole of the dissolved material per liter of water (35). Thus, if the Venus

For instance, a 1.7M/l solution of 6M HCl has $n=1.45$. Thus, if the Venus aerosols contained a few moles per liter of dissolved salts, their indices of refraction would have the required value. Exactly the same situation occurs in terrestrial water aerosols. Water has an index of refraction of 1.33; however, the scattering properties of these particles can be well-accounted for by Mie theory using an index of refraction of 1.50 rather than 1.33 (23). The large refractivity is due to both dissolved salts and the insoluble portion of the nuclei. Thus a value of 1.45 for Venus hydrochloric acid aerosols is eminently reasonable.

Vapor Pressure of Water

The partial pressure of H_2O vapor in a gas containing suspended aerosols will in general not be the same as the tabulated value of the vapor pressure, which refers to the ^{equilibrium} partial pressure over a flat, infinite surface of pure water. The growth of aerosol particles and their equilibrium vapor pressure depends on a number of factors, including the size, shape, and wettability of the nuclei, surface tension, and the concentration of dissolved salts (22, 24). In particular, the partial pressure of water in a solution is reduced in proportion to the mole fraction of solute, in accordance with Raoult's Law, so that it is possible for aerosols to grow under conditions where the partial pressure of water is less than half the vapor pressure at that temperature. However, the Raoult's Law effect is probably not capable by itself of reconciling the Venera and earthbased measurements, nor would it allow the formation of water aerosols if H_2O mixing ratios of 10^{-6} are typical.

The UV Clouds

To the eye the disk of Venus is featureless, but when the planet is observed in wavelengths below 0.4μ large diffuse markings, which persist for several days or weeks, become visible. Since the apparent rotation period of the UV features is of the order of 5 days, while the solid body of the planet rotates with a 243 day period, the markings obviously are atmospheric rather than surface features.

Dollfus (36) and Kuiper and his associates (37) have published a large number of photographs of these clouds. A natural explanation in terms of the model discussed here is that the markings reflect variations in the intensity of the ferric band.

Several lines of evidence indicate that the ^{UV} features are associated with a partially transparent or incomplete cloud or haze layer, which ^{scatters light but only} absorbs weakly in the UV and which overlies a more strongly UV-absorbing cloud deck. 1. The UV features are seen more often near the center of the disk ~~rather~~ than near the polar or equatorial limbs. 2. The markings occur more frequently at smaller phase angles than at large (38). 3. The ratio of the reflectivity of Venus in the UV to that in the visible is considerably higher at larger phase angles than at smaller (11). 4. The minimum at 0.34μ which is apparent in Glushneva's spectrum at a phase angle of 45° , seems either to have disappeared or to have shifted to shorter wavelengths in the 87° spectrum.

A decreased strength of the near-UV ferric band could be due to lower concentrations of either Fe^{+3} or HCl or both in the upper haze layer. Such a decrease may reflect more favorable conditions for the condensation of H_2O vapor at higher altitudes due to the lower temperatures. Alternatively, larger iron concentrations at lower altitudes could be due to increases in the supply of silicate dust from volcanic eruptions on the surface. Physically, the UV features could be either holes, local deficiencies of iron in the upper clouds, or local concentrations of iron in the lower clouds, possibly related to the surface distribution of active volcanoes.

~~PP Somewhat tentative additional support for the present model can be found in the~~
~~In the far IR spectrum of Venus~~
~~for IR spectrum of Venus.~~ Three minima appear to be present at 8, 9.5, and 11μ . The 9.5μ depression is probably due to a CO_2 band at 9.4μ , although there is no sign of a minimum at 10.4μ , where another CO_2 band is located. The 8μ feature may be a hydrochloric

acid absorption band. The 11μ and possibly the 9.5μ minima may be associated with silicate ~~or carbonate~~ aerosol nuclei. Silicates possess emissivity minima in the $9-11\mu$ range due to the Si-O vibration band. The band location is composition-dependent, being shifted toward 9μ for acidic rocks and toward 11μ for ultrabasic silicates; carbonates also have an emissivity minimum at 11μ (39).

In order for ~~the~~ silicate ~~carbonate~~ bands to be seen in emission these materials would have to be abundant at the level from which the thermal radiation originates. However, the hydrochloric acid band ^{must be} seen in absorption, ^{which requires} ~~implying~~ a relatively lower silicate and higher HCl concentration at greater altitudes. Thus the UV markings and the thermal IR bands may be closely associated, and simultaneous monitoring of Venus in these two spectral regions may prove highly informative.

Finally, it must be stressed that these conclusions apply only to the visible clouds. Other substances may be important in the lower atmosphere.

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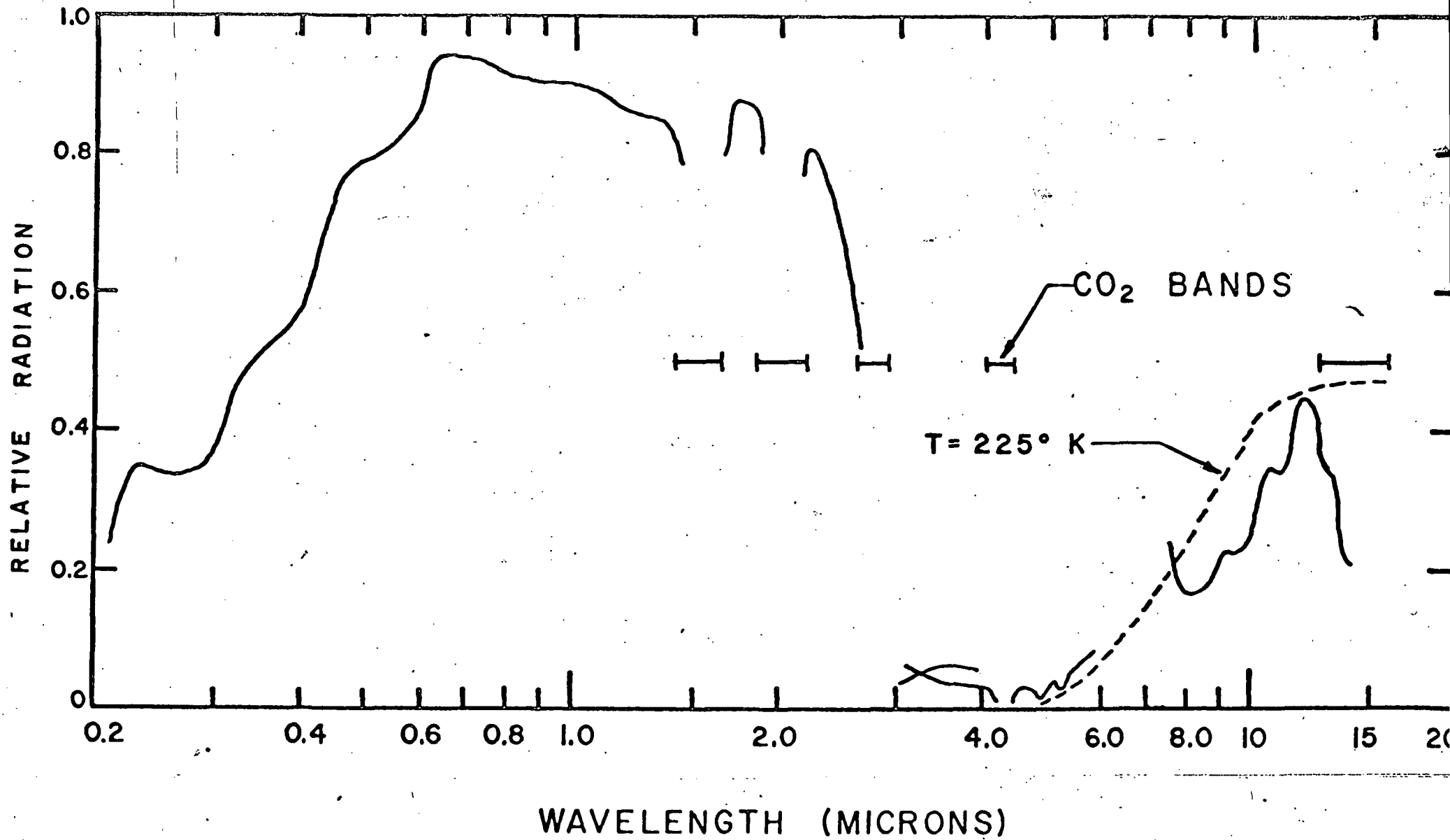
FIGURE CAPTIONS

Figure 1. Relative reflectivity and thermal emission spectrum of Venus. The following sources have been used to construct this spectrum: $< 0.3\mu$ (10), $0.3 - 1.0\mu$ (11), $0.8 - 1.2\mu$ (12), $1.2 - 3.5\mu$ (13, 2), $3.0 - 14\mu$ (14, 15). The near-UV and near -IR values have been normalized to the Bond albedo values of Irvine et. al. (11); the far-IR curve has been arbitrarily joined to the near IR curve at 3.2μ . The bars indicate the position of strong CO_2 bands in the atmosphere of Venus. A strong H_2O band in the Earth's atmosphere occurs at $6 - 7.5\mu$ and an ozone band at 9.8μ .

Figure 2. Transmission spectra of H_2O and 6M HCl. Absorption cell thicknesses: $0.2 - 0.7\mu$, 1 cm; $0.7 - 2.5\mu$, 40μ ; $2.5 - 16\mu$, 5μ . The $2.5 - 16\mu$ data was adapted from (19) and (20), the $0.2 - 2.5\mu$ data was measured on a Carey 14 spectrophotometer. Also shown is the reflection spectrum of an artificial basaltic glass powder of composition approximating lunar Apollo 11 samples (this spectrum has been multiplied by 3) and the transmission spectrum of a solution resulting from leaching this glass with 6M HCl for 60 hours (cell thickness 0.1cm).

Figure 3. Near-UV spectrum of Venus and absorption spectra of ferric ions. Top: Relative reflectivity spectrum of Venus by Glushneva (28), as reduced by Cruikshank and Thompson (12). Bottom: absorption spectra of Fe^{+3} ions in various hydrochloric acid solutions (29), and of FeCl_3 . (Absorbance is proportional to the negative logarithm of transmittance. To avoid confusion the absorbance spectra have been displaced in the vertical direction by arbitrary amounts.) The spectrum of Fe^{+3} in H_2SO_4 solutions is ~~very~~ similar to the H_2O curve.

VENUS SPECTRUM



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